PYROELECTRIC RESPONSE OF FERROELECTRIC PVDF AND THEIR COPOLYMER: A REVIEW

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ABSTRACT

The world's conventional energy sources are fast depleting due to population growth and civilization expansion. Subclasses of piezoelectric materials include ferroelectric and pyroelectric materials. Materials with permanent polarization as a result of their chemical composition are called ferroelectric materials. However, the spontaneous polarization that happens in pyroelectric materials when they are exposed to temperature changes. With the use of ferroelectric, pyroelectric, and piezoelectric materials, waste environmental energy is mainly transformed into electrical energy. Modern electronics are designed with reduced power consumption in consideration. Materials based on polymers are thought to be viable options for these devices. Because of its low thermal conductivity and permittivity, flexibility, processability, greater output performances, and affordability, PVDF and its family of polymers(copolymer & terpolymer)are widely employed in device applications.

KEYWORDS: Ferroelectric, Pyroelectric, Piezoelectric, PVDF, Copolymer, Terpolymer

1. INTRODUCTION

Certain natural materials have permanent polarization in their crystal structure, meaning that external factors like pressure, temperature, or electric field don't affect them.The material is known as "ferroelectric material". Furthermore, when exposed to temperature fluctuations, certain crystals have been shown to display spontaneous electric polarization. The term "pyroelectricity" refers to this phenomena of temperature-dependently induced electric polarization, while the term "pyroelectric materials" refers to the substances that exhibit this response. Ferroelectric materials exhibit permanent polarization and, in accordance with the direction of the electric field being reversed, also reorient their dipole and direction of polarization. All pyroelectric materials do not necessarily need to be ferroelectric, despite the well known fact that all ferroelectric materials are pyroelectric. A pyroelectric action could be prevented by the high coercive field that could exceed the limit of electrical breakdown or by the intrinsic asymmetry in the crystal structure that prevents polarization reversal.

Joseph Vasalek discovered the phenomena of ferroelectricity in 1921 while studying the dielectric characteristics of sodium potassium tartrate tetrahydrate (NaKC4H4O6.4H2O). He claimed that fundamental state of this material is permanent polarization[1].One or more ferroelectric phases, which exhibit a spontaneous polarization that can be realigned by applying an external electric field, are the defining characteristics of ferroelectric crystals [2].Ferroelectric hysteresis is a nonlinear fluctuation in polarization with electric field that occurs when an electric field is applied to a ferroelectric material [3]. The phase transition temperature, often known as the Curie temperature (TC), is another significant property of ferroelectric materials. The crystal displays ferroelectricity (ferroelectric phase) at temperatures below TC, and vice versa at temperatures above TC, where the ferroelectricity disappears and the crystal changes to a paraelectric phase[2,4]. Since the lattice symmetry in the ferroelectric phase is reduced, it is generally accepted that the ferroelectric phase results from a deformation of the paraelectric phase structure of a crystal [2]. Ferroelectric transition temperature, ferroelectric hysteresis,and spontaneous and reversible polarization are the three primary characteristics of a ferroelectric material[3]. Ferroelectric materials belong to the subclass of pyroelectric materials, which in turn also belong to the subclass of piezoelectric materials. Consequently, pyroelectric and piezoelectric actions are displayed by ferroelectric materials [3].The ideas of pyroelectricity, piezoelectricity and ferroelectricity are intimately related for their crystalline nature [5]. 11 of the 32 classes of crystals that also called point groups, are not ferroelectric because of absence of polarity and also they have a centrosymmetric center of symmetry. 20 of the remaining 21 crystal classes are noncentrosymmetric, and one exhibits no piezoelectric action. 10 of these 20 groups, known as pyroelectrics, have a single polar axis and spontaneously polarised in response to temperature. The amplitude of the dipole moment varies with temperature.Ferroelectric pyroelectric crystals are differentiated from other types by having a persistent dipole that can be flipped in response to an external electric field [3, 5, 6]. Figure 1 depicts the 32 crystal classes categorized by their pyroelectric, piezoelectric and ferroelectric characteristics.

Because pyroelectric materials display spontaneous polarization, which can be reduced by heating the material, they can be used as infrared radiation sensors [3]. In the second half of the 20th century, research on the pyroelectric, piezoelectric and ferroelectric effects of materials emerged and found expanding applications [6].

Since ferroelectric materials are more sensitive to changes in the environment than other types of materials, ferroelectric

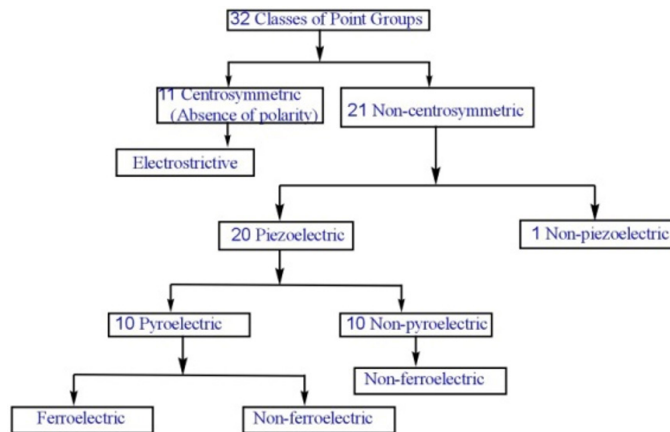materials are used in the majority of practical pyroelectric and piezoelectric instruments [3].

Figure: 1 Classification of crystal classes according to their piezoelectric, pyroelectric and ferroelectric properties.

In 1969, Kawai reported on his finding of piezoelectricity in poly(vinylidene fluoride) (PVDF) [7]. Two years later, pyroelectricity in the same polymer was discovered [8]. Over the past few decades, major scientific and technical advancements have been made possible by the polymer family of PVDF. Particularly, applications have made extensive use of the homopolymer PVDF and its copolymer poly(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE) [9]. PVDF and its copolymers exhibit the most well-known electroactive properties [10] among polymeric materials [10], making them the superior option for smart material applications in a variety of fields, including biomaterials [11], sensors [10,12], ultrasonic transducers[12], actuators[10], transducers[12], energy harvesters [13], and energy storage systems[14]. While PVDF and P (VDF TrFE) exhibit lower pyroelectric and piezoelectric coefficients than lead zirconate titanate (PZT), they nonetheless offer the benefits of low thermal conductivity and permittivity, good impedance matching to water and air, softness, flexibility, and processability, as well as being relatively inexpensive [15,10].

Electroactive polymers are the most attractive family of polymers that are utilized as smart materials in a variety of applications, such as energy-harvesting devices, actuators, sensors, and so on [10]. The scientific community has placed a great deal of emphasis on ferroelectric polymers because of their potential for use in the next era of electronic devices and energy applications. The ferroelectric phenomenon in polymers was discovered by Kawai in 1969 [16], which sparked a lot of research and interest in soft materials and resulted in a wide range of applications.

Pyroelectric activity can be found in a wide range of piezoelectric, ferroelectric, and non-ferroelectric materials, but for the sake of this review, PVDF and its copolymer, as well as their pyroelectric activity, enrgy storage phenomenon are solely addressed here.

2. THE PYROELECTRIC EFFECT

Since pyroelectric materials are all polar, they all show spontaneous polarisation (Ps) when no external electric field is applied. Every surface of the material has a charge due to the spontaneous polarisation that occurs within it, and free charges, such as ions or electrons, are drawn to the charged surfaces. When the ambient temperature is altered, the behaviour of the surface charge can be used to understand the origin of pyroelectric behaviour, provided that the polarisation level is dependent on the temperature of the material. A heated pyroelectric (dT/dt > 0) loses some of its spontaneous polarisation because thermal vibrations cause the material's dipoles to become disoriented; this is illustrated in **Figure. 2**. A decrease in the amount of free charges attached to the material surface results from this drop in the polarisation level [17]. In the event of an open circuit, an electric potential is created across the material since the free charges stay at the electrode surface [18]. An electric current flows between the two polar surfaces of the material when it is subjected to short circuit circumstances.
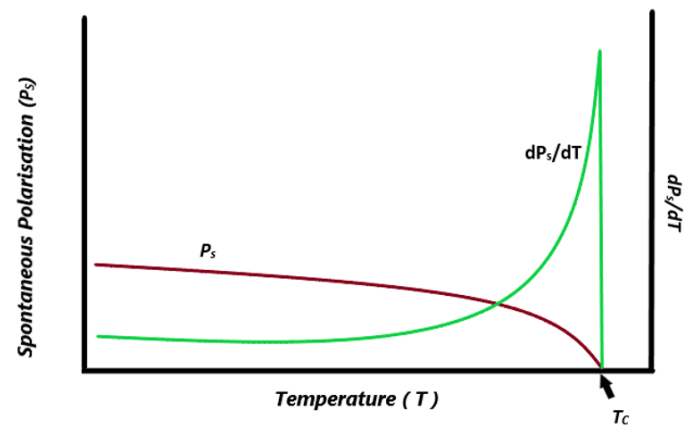

Figure:2 Dependence of spontaneous polarization (P_s) and pyroelectric coefficient (dPs/dT) on temperature (T) of a ferroelectric material.

Similarly, when the pyroelectric cools down (dT/dt < 0), the dipoles reorient and the amount of spontaneous polarisation rises. This causes the electric current to reverse under short-circuit conditions because free charges are drawn to the polar surfaces.

Equation (1) shows the correlation between pyroelectric charge (Q), pyroelectric current (ip), rate of temperature change (dT/dt), material surface area (A), and pyroelectric coefficient (p) [19] under short circuit condition.

$$i_p = \frac{dQ}{dt} = pA\frac{dT}{dt} \qquad (1)$$

$$p^{\sigma,E} = \left(\frac{dP_s}{dT}\right)_{\sigma,E} \qquad (2)$$

On the other hand, equation (2) shows the pyroelectric coefficient of an unclamped material, under constant stress and electric field, where 'P_s' is spontaneous polarisation [20], and subscripts 'σ' and 'E' correspond to conditions of constant stress and electric field respectively. Small temperature

variations can generate a pyroelectric current ,which has been used for motion detection by body heat and infrared imaging [17]. This small current may also be used for energy harvesting purposes. It is obvious from equation (1) that a pyroelectric device with a large surface area, a high pyroelectric coefficient, and a high rate of temperature change would maximise the pyroelectric current under short-circuit conditions. Gaugain in 1859 showed that the generated current according to equation (1) is only connected to the surface charge and proportional to the surface area (A) and is independent of its thickness [21].

Every pyroelectric material is piezoelectric because all pyroelectric materials must be polar and show some degree of polarisation (pyroelectrics are a sub-class of piezoelectric materials such that all pyroelectrics are piezoelectric). But not all piezoelectrics are pyroelectric because some materials, like quartz, only polarise when subjected to mechanical stress.

By changing the applied electric field's direction, the orientation and sign of spontaneous polarisation in "ferroelectric" pyroelectric materials can be changed .Since all ferroelectrics are pyroelectric and piezoelectric in the same way, these materials form a subclass of pyroelectric materials. When heated above the Curie temperature (T_c), ferroelectric materials experience a phase transition in which both the pyroelectric and piezoelectric behaviour, as well as spontaneous polarisation, disappear. In general, ferroelectric materials have higher pyroelectric and piezoelectric coefficients than non-ferroelectric materials.

Figure 2 illustrates how a ferroelectric's spontaneous polarisation reduces as temperature rises and how the pyroelectric coefficient (dP_s/dT) that corresponds to this decrease .The material starts to rapidly lose its polarisation as it gets closer to T_c, which causes the pyroelectric coefficient to climb significantly. The phase transition at the Curie temperature has drawn some interest for pyroelectric harvesting since the material has the potential to discharge a large amount of electrical energy as the level of polarisation falls to zero.

2.1 Primary, secondary and tertiary pyroelectric coefficients
As was previously mentioned, a temperature shift modifies the degree of polarisation and produces an electric current. The situation of a perfectly clamped material under uniform strain [17], with a homogenous heat distribution and no external field bias, is relevant to the primary pyroelectric effect. Thermal expansion causes a strain that modifies the electric displacement through the piezoelectric effect, which is why a secondary pyroelectric effect is frequently seen in measurement and energy harvesting scenarios. Lubmirsky et al. have extensively documented the difficulty of distinguishing between pyroelectric and piezoelectric responses [22]. The relation of the primary pyroelectric coefficient at constant strain (p^x) in a clamped condition with the pyroelectric coefficient at constant stress (p^σ) is shown by equation (3) using tensor notation [23,21,24,25].

$$p^{\sigma,E} = p^{x,E} + d_{ij}c_{ij}^E\alpha_i^E \qquad (3)$$

Where d_{ij}, c_{ij} and α_i^E are stands for piezoelectric coefficient, elastic constants and thermal expansion coefficient respectively under constant strain (x). The term $d_{ij}\,c_{ij}^E\,\alpha_i^E$ is known as the secondary pyroelectric coefficient. The overall pyroelectric coefficient can be significantly influenced by it, even if it can be small in ferroelectrics [23].

2.2 Pyroelectric stored energy
The following formulae can be used to derive the charge and voltage created as well as the energy stored in an unclamped pyroelectric material: According to equation (1), the pyroelectric current solely depends on the electrode's effective area and is not affected by the thickness of the material. The net charge created as a result of a temperature change (ΔT) is

$$Q = p\,A\,\Delta T \qquad (4)$$

which may be obtained by integrating equation (1) with respect to time. Since in most of the cases pyroelectric materials are dielectric, equation (5) represents the equivalent capacitance (C).

$$C = \frac{A\varepsilon_{33}^\sigma}{h} \qquad (5)$$

where ε_{33}^σ is the permittivity at constant stress. The expression of the open circuit voltage (V) and electric field (E) that are created across the electrodes are shown by equation (6) and (7) respectively from equation (4) and (5).

$$V = \frac{p}{\varepsilon_{33}^\sigma}\,h\Delta T \qquad (6)$$

$$E = \frac{p}{\varepsilon_{33}^\sigma}\,\Delta T \qquad (7)$$

The amount of energy stored in a pyroelectric material at the end of the process is shown by equation (8) according to the equation of stored energy $E = \frac{1}{2}\,CV^2$ in a capacitor.

$$E = \frac{1}{2}\frac{p^2}{\varepsilon_{33}^\sigma}\,Ah(\Delta T)^2 \qquad (8)$$

3. FERROELECTRIC PYROELECTRIC POLYMER (PVDF AND ITS COPOLYMER)
A class of materials known as ferroelectric polymers exhibit reversible spontaneous electric polarisation under the application of an electric field [26].

Ceramic materials and single crystals were the first materials in which the piezoelectric phenomena was found. Kawai discovered the pyroelectricity of poled PVDF in polymers two years after discovering its piezoelectric characteristics [27]. It wasn't until 1978 that Kepler and Anderson confirmed the ferroelectric characteristics of PVDF [28]. With its interesting physical and chemical characteristics, including its compact structure, large permanent dipole moment, chemical stability , ease of manufacturing [29], and low annealing temperature [30], PVDF has earned the title of "ferroelectric polymer" par

excellence. PVDF can also be produced in polymer blends, by combining it with inorganic materials to generate composites, and by employing other processing techniques, such as melt and solvent procedures.

Since PVDF and its copolymers, such as P(VDF-TrFE), poly (vinylidene fluoride-co-hexa-fluoropropene) (PVDF-HFP), or poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE), have been increasingly relevant in electroactive polymer research and application [10]. While PVDF is the most well-known example of a ferroelectric polymer, over the past years, a great deal of research has been done on other polymers that exhibit intriguing ferroelectric characteristics. These polymers include ferroelectric liquid-crystal polymer, cellular ferroelectret polymer blends and composites, polyamides, cyanopolymers, copolymers, and terpolymers based on PVDF, polyureas, and polythioureas, as well as biopolymers such as polypeptides and cyanoethyl cellulose [26, 31, 32].

Polymers' molecular structure and orientation are responsible for their ferroelectric characteristics. When compared to single crystals or ceramics, polymers' mechanical qualities, such as their light weight and flexibility, are advantageous for the production of sensors and actuators. Consequently, these organic ferroelectric materials open up new possibilities for actuators, capacitors, piezo- and pyroelectric sensors, memory, and other devices [26].

Specifically, the polymer's molecular structure must contain dipoles, and these dipoles must be reoriented within the material and maintained in their preferred orientation state. This reorientation is accomplished through the use of a poling process method [33]. Amorphous polymers can also present piezoelectric effects if their molecular structure contains strong molecular dipoles; however, they typically show a lower piezoelectric response than semicrystalline polymers.

The materials other than ferroelectric that exhibit pyroelectricity are zinc oxide (ZnO), cadmium sulphide (CdS), aluminium nitride (AlN), and gallium nitride (GaN) etc.

3.1 PVDF

PVDF's chemical formula ($—CH_2— CF_2—$) is a transitional structure between polyethylene (PE) ($—CH_2—CH_2—$) and polytetrafluoroethylene ($—CF_2—CF_2—$). It offers the main-chain structure of PVDF some stereochemical constraints, identical to polytetrafluoroethylene (PTFE), as well as high flexibility, identical to polyethylene (PE) [31]. PVDF has distinct molecular and crystal structures as a result of its structural properties, which vary according on the material's processing circumstances [10].

With a degree of crystallinity usually between 50 % and 60%, PVDF can be easily prepared from gaseous monomers 1,1-difluoroethylene by free radical polymerisation [26]. The Chemical structure of PVDF's $\alpha, \beta,$ and γ phases are shown schematically in **Figure 3**. PVDF is a semicrystalline polymer with five unique crystalline phases associated with various chain conformations: TG$^+$ TG$^-$ (trans-gauche-trans-gauche)

for the α and δ phases, TTTG$^+$ TTTG$^-$ for the γ and ϵ phases, and all trans (TTT) planar zigzag for the β phase [10,26]. Particularly for sensor or actuator application devices,the primary characteristics of PVDF are associated with the PVDF monomer unit's significant electrical dipole moment($5-8\times10^{-30}$ C.m), which is brought about by the carbon and fluorine atoms' high electronegativity [10]. Subsequently,regular molecular chain packing that prevents internal moments from cancelling out produces the electric polarisation of PVDF in crystals. According to reports,PVDF films in the β phase have piezoelectric coefficients as high as -34 pCN^{-1}, which is higher than any other polymer's recorded values. PVDF is a polymer that is stable over heat , with a glass transition temperature (T_g) that is close to 40^0 C [34].

In terms of dipolar moment per unit cell (8×10^{-30} C.m) [10], the β phase of the PVDF exhibits the highest . Moreover, it has the largest piezoelectric, which finds extensive use in sensors [1], actuators [31], batteries, biomedical applications [35], and self-powered devices [36], among other energy-harvesting applications [37].

The dipolar moments between the two antiparallel chains within the unit cell self-cancel, resulting in the macroscopically nonpolar α and ε phases of PVDF [10,26]. There have been many processing approaches utilised to generate the β phase of PVDF [29]. The most used technique is the α to β phase transition, which is accomplished by mechanically stretching the molecules to align the molecular chains at low speed and low temperature between 80 and 140^0C [10] . The samples are then poled under a few hundred MV m^{-1} electric field at a regulated temperature. Also, the use of fillers that can function as electroactive phase nucleating agents is one of the several methods utilised to generate β-PVDF [10].
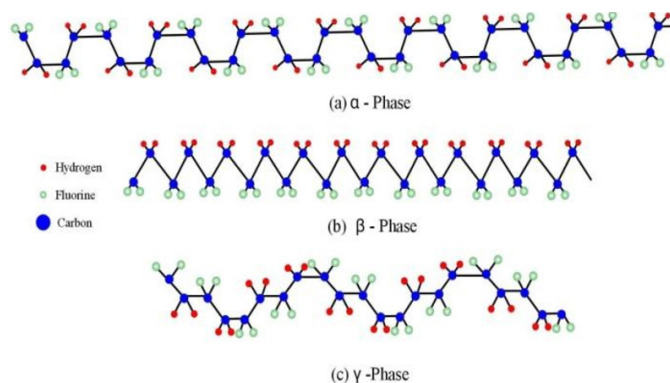

Figure:3 Schematic chain conformation of PVDF[(a) α - phase, (b) β - phase and (c) γ- phase]

3.2. PVDF-Based Copolymers

It is possible to adjust the molecular structure of PVDF to customise intermolecular interactions and, consequently, change the polymer's overall characteristics. Currently, a number of innovative PVDF-based copolymers and terpolymers with unique behaviours in response to electric fields are produced by utilising such alterations.

3.2.1. P(VDF-TrFE)

P(VDF-TrFE), shown in **Figure 4**, is the most researched and utilised PVDF copolymer. In 1980, the ferroelectric phase-transition of this copolymer was found [31]. When the VDF content is between 50% and 80%, the addition of TrFE co-monomer causes the material to crystallise in the ferroelectric crystalline β phase [10,38]. As a result, the copolymer crystallises in the β phase directly, bypassing the thermos-mechanical procedures that are typically used with PVDF samples [38].

The two monomers VDF and TrFE are polymerised using free radicals to create P(VDF-TrFE) [12]. P(VDF-TrFE) exhibits more remnant polarisation in comparison to PVDF because of the preferred orientation of the well-grown crystallites' and high degree of crystallinity [12]. A higher electromechanical coupling factor from the oriented crystal gives P(VDF-TrFE) a higher mechanical-to-electrical transformation efficiency, or vice versa.

The copolymer's transition temperature is influenced by the molar ratio of TrFE; it decreases to $130^{0}C$ as the molar ratio increases between 55 and 88 mol % [10]. The mechanical characteristics, dielectric constant, and dielectric losses of PVDF and P(VDF-TrFE) are similar; however, the piezoelectric coefficients, d^{33} and k^{33}, in the copolymer are higher than those of pure PVDF [33].
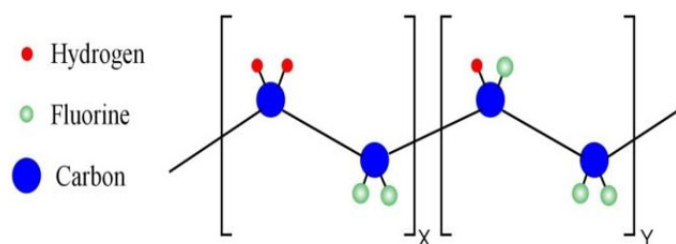

Figure:4 Schematic chain conformation of P(VDF-TrFE)

3.2.2. PVDF-CTFE

The P(VDF-CTFE) copolymer is produced when CTFE is added to the polymer chain of PVDF that is shown in **Figure 5**.

The copolymer's final qualities are rely upon the amount of polychlorotrifluoroethylene (PCTFE) present, and the copolymer's glass transition temperature shifts from $-40^{0}C$ for PVDF to $-45^{0}C$ for PCTFE [10]. Only when the CTFE level is less than 16 mol % can the copolymer be formed in a semicrystalline condition; at larger CTFE concentrations, the material is invariably in an amorphous state [39]. When compared to pure PVDF, P(VDF-CTFE) exhibits improved dielectric constant, greater electrostrictive strain response, and optimised d33 approximately -140 pC N^{-1} [10,40]. Bulky CTFE causes the structure to become looser, which facilitates dipole orientation under an external electric field.
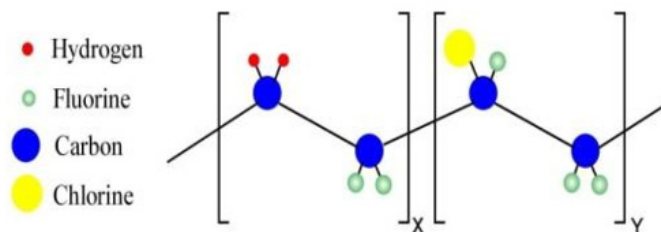

Figure: 5 Chemical structure of P(VDF-CTFE)

3.2.3. P(VDF-HFP)

As hexafluoropropylene is introduced with the PVDF polymer, the copolymer P(VDF-HFP) is produced, as shown in **Figure 6** [41]. P(VDF-HFP) is chemically inert and exhibits a reduced degree of crystallinity between the PVDF and its copolymers [10]. The greatest remnant polarisation, which is obtained after processing by solvent casting, can reach up to 80 mC m^{-2} for low HFP values of about 5%, and it decreases as the HFP content increases [10]. The ferroelectric characteristics of this copolymer are fundamentally dependent on the processing parameters. P(VDF-HFP) exhibits a $d_{31} \approx -30$ pC N^{-1} piezoelectric coefficient, which is increasingly valuable for ferroelectric and piezoelectric device applications [10].
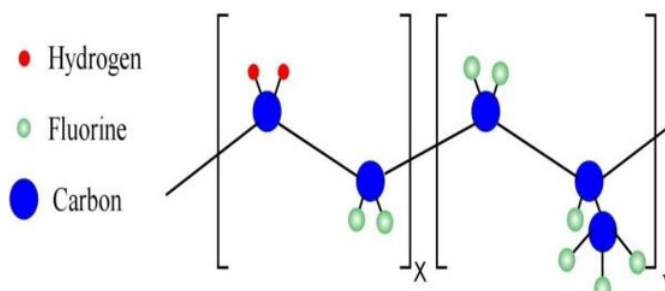

Figure: 6 Chemical structure of P(VDF-HFP)

3.2.4. P(VDF-TrFE-CTFE)

Terpolymers have the potential to enhance polymers' electromechanical and dielectric constants, which are essential for a variety of uses, including as the energy and electronics sectors. After adding CTFE to P(VDF-TrFE), poly vinylidenefluoride-trifluoroethylene-chlorotrifluoroethylene (P(VDF-TrFE-CTFE)) is obtained **Figure 7**. Because of its larger dielectric constant than other PVDF-based polymers, high polarisation, high electromechanical response, and elastic energy density, it is considered to be a very promising ferroelectric material [42]. P(VDF-TrFE-CTFE) is especially interesting for the growth of devices based on extremely efficient electromechanical performance and a lack of deterioration resulting from dielectric leakage because of these combined features [42].

There are numerous applications for PVDF and its copolymers, which are the primary semicrystalline electroactive polymers [31]. Additionally, a lot of work has gone into creating novel organic polymers with attractive ferroelectric, piezoelectric, and pyroelectrical properties [31]. While none of these materials have yet to reach the piezoelectric qualities found in PVDF-based polymers, the new materials might have other benefits,

such as significantly higher operating temperatures and possibly novel methods for film or device-forming. These substances include biopolymers, aromatic polyamides, polyureas and polythioureas, cyanopolymers, and odd-numbered nylons [38].
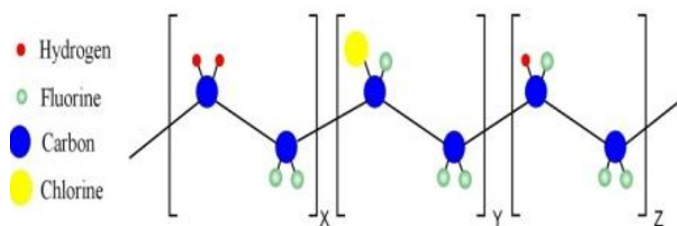

Figure: 7 Chemical structure of P(VDF-TrFE-CTFE)

4. CONCLUSION

The history of the pyroelectric effect in PVDF polymers and their families was compiled in this review. After a brief overview of the ferroelectric and pyroelectric phenomena, pyroelectric polymers and their energy-storing capacity were discussed. The chemical structures of PVDF, its copolymer, and its terpolymer were also covered in this review, along with a brief discussion of the dipole moment's presence in each of their structures. PVDF and its family-based materials are widely used in device applications because of their inherent qualities, which include low thermal conductivity, flexibility, processability, and affordability, especially considering the low power consumption of current devices.

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